Diffusion Barriers Between Gold and Semiconductors

COMPARISON OF RF DIODE SPUTTERED TITANIUM-TUNGSTEN AND DC MAGNETRON SPUTTERED TUNGSTEN BARRIERS BETWEEN GOLD AND SILICON

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The effectiveness of a number of semiconductor devices depends on the efficiency with which interdiffusion between the semiconductor and metals, which must be applied to it either as contacts or conductive metallizations, can be blocked. Comparisons of the characteristics of the diffusion barriers which can be used between gold and semiconductors — such as those which are made here — therefore have considerable significance.

The use of refractory metals as thin film 'diffusion barriers' in semiconductor technology has been widely reported upon (1). In some structures, the barrier is used as a Schottky barrier contact directly on *n*- or *p*-type silicon and usually has an overlying film of solderable or bondable metal, for example gold or aluminium, which also provides low-resistivity interconnections.

In other structures, the barrier is employed to minimize or reduce the interdiffusion between an underlayer, such as aluminium, and an overlayer, such as gold (2). Also, barriers have been applied as adhesive layers to silicon or ceramic dice in conjunction with a solderable or bondable overlayer of gold, silver or nickel, for example. This structure allows the attachment of such dice to packages or carriers by 'eutectic' or solder bonding.

These thin films of refractory metals have not always performed well as diffusion barriers (3), and this has led to controversy as to the deposition parameters which actually govern their barrier properties, and even as to whether barrier behaviour in service can be predicted with any degree of confidence at all. For example, the value for the energy of activation which governs the rate of diffusion of aluminium through relatively pure radio frequency (RF) diode sputtered $Ti_{33}W_{67}$ thin films has been calculated to be 0.6 eV (4). This implies that, in terms of the Arrhenius relationship, interdiffusion should be complete at room temperature in about three years and that if such films were used as contacts in Schottky diodes, the latter would develop electrical instability in storage even at room temperature! When one considers that much of the early work with refractory metal diffusion barriers was done in vacuum systems having typical 'base' pressures as high as 10^{-3} Pa (10^{-5} torr) (5), and that arrival rates of oxygen or nitrogen at a substrate surface at such pressures are several atomic layers per second, it is not surprising that difficulties in the reproducibility of resultant film properties have arisen. Moreover, early workers did not have analytical tools at their disposal with which to investigate the purity and other characteristics of the films they produced. It was nevertheless surprising to find that near-stoichiometric molybdenum oxynitride was produced by the RF sputter deposition of molybdenum in pure argon at base pressures of about 1.3 mPa (1×10^{-5} torr) (6). This discovery would probably not have been made without the use of nuclear microanalysis. More recently, the sensitivity and resolution of other analytical techniques such as Auger electron spectroscopy (AES), electron spectroscopy for chemical analysis (ESCA) and secondary ion mass spectrometry (SIMS) have been developed to the point where they can be used to perform quantitative analysis of trace impurities in thin films with high confidence.

The realization that the barrier properties of refractory metal thin films are strongly dependent upon the impurities introduced into them during their deposition evolved slowly at first (7), but accelerated as the new techniques became available for studying the manner in which the low concentrations (0.1 to 1 atomic per cent) of elements such as oxygen or nitrogen, needed to improve their properties, were incorporated in refractory metal films. It has emerged as likely that these elements concentrate preferentially, in the form of interstitial alloys or compounds with the depositing metal, within the grain boundaries of this metal, and thereby impede the movement of diffusing species along these boundaries. Since the grain boundary volume is determined to a large extent by crystallite size, one can estimate approximately the concentration of impurity atoms needed to saturate the grain boundaries. For example, crystallites about 30 nm in size would require less than one atomic per cent of an impurity to fill the grain boundary voids. One can therefore understand the difficulties involved in controlling the concentrations of impurities present under typical deposition conditions. Thus, an aura of 'black art' concerning the barrier properties of refractory metals has persisted even to recent times. However, Holloway and Nelson (8), and more recently Dalal *et al.* (9) discovered that the barrier properties of refractory metal thin films improved with the controlled introduction of oxygen or water vapour into the films during the evaporation procedure. Holloway postulated that the improvement in barrier properties was due to 'capping' of the grain boundaries.

With sputter deposition, there generally exists a 'shadow region' near the periphery of the deposition zone, where film darkening can be observed. This darkening is associated with a 'gettering' phenomenon, in which 'reactive sputtering' occurs and gaseous impurities in the vacuum system can combine chemically with the depositing metal. Thus, increased residence time within this zone causes an increase in the degree of impurity

incorporation in the resultant film.

This 'gettering' effect could be expected to improve the barrier properties of refractory metal films deposited in the shadow region. This study describes some recent observations made in this connection, which demonstrate that deposition configuration indeed strongly determines resultant barrier properties. They also show that direct current (DC) magnetron sputtered tungsten, deposited in pure argon with substrate rotation into and out of the deposition zone, is a far better diffusion barrier than RF sputtered titanium-tungsten deposited in the static mode (7). Additionally, analytical data are reported which support a proposed model of the deposition parameters governing their barrier properties.

Experimental Procedures

All sputter depositions were carried out in a Perkin-Elmer Model 4400 deposition system equipped with a 65 cm diameter rotating substrate holder, load lock, in-chamber Meissner (liquid nitrogen) trap and cryopump. The base pressure prior to each deposition was typically less than 50 μ Pa (10^{-7} Torr). It increased almost ten-fold in the 'throttled' mode prior to argon admission. The sputtering pressure was typically 1.33 Pa (10^{-2} Torr) of 99.99 per cent purity argon. Both titanium-tungsten ($Ti_{33}W_{67}$) and tungsten were sputtered by the DC magnetron technique from 20 cm diameter targets of 99.9 or 99.99 per cent purity at 2 kW power while rotating at 5 rpm. This resulted in a deposition rate of about 25 nm/minute for both materials. The RF diode sputtered titanium-tungsten and gold system referred to below was deposited as described in a previous publication (4). Prior to the deposition of each film, the substrates were sputter etched at 1 kW for one minute for the purpose of removing 'native' oxides.

The substrates were (100) *p*-type polished silicon wafers (1 to 10 ohm cm) taken directly from a nitrogen-filled 'clean pack' and not subjected to further chemical cleaning.

The typical deposited thicknesses for titanium-tungsten and tungsten films, as measured by profilometry of steps on a silicon monitor wafer etched with 30 per cent hydrogen peroxide at 60° were about 200 nm, whereas the thicknesses of the gold films, which were etched in saturated iodine-potassium iodide solution, were typically about 150 nm. Film resistivity, as measured by a four-point probe, was about 90 μ ohm cm for titanium-tungsten and about 30 μ ohm cm for tungsten.

Auger surface and depth profile analyses were carried out with a Physical Electronics Model 590 scanning Auger microprobe. The elemental sensitivity factors reported by Davis *et al.* (10) were used to quantify the spectra.

Results

The gold/titanium-tungsten metallization, deposited by RF diode sputtering on silicon, has been described in prior work (7). It exhibited extensive interdiffusion between the gold and silicon substrate after heat treatment for 30 minutes at 300°C. Its behaviour was comparable with that of gold/titanium-tungsten deposited by RF diode sputtering on aluminium-copper alloy (4). The energy of activation for the interdiffusion reaction in both metallization systems is about 0.6 eV.

Samples of DC magnetron deposited gold/tungsten on silicon were heated at 300°C for 30 minutes in nitrogen. Figure 1 shows the Auger depth profiles of the as-deposited and heat treated samples. From these profiles it can be concluded that little, if any, interdiffusion occurred even after short excursions to 600°C for 5 minutes followed by rapid quenching to room temperature.

Similar results were obtained for gold/titanium-tungsten films deposited on silicon in an identical manner. However, one problem which became evident after several gold/titanium-tungsten depositions was the appearance of visible particles on the substrates. Subsequent Auger analysis of these particles revealed that they consisted of titanium plus tungsten. Their origin is unknown at present, but it is suspected that the uniformity shaper and 'ground' shielding surrounding the titanium-tungsten target are involved in their formation. It is important to note that no such problem was observed for the gold/tungsten metallizations after a comparable number of depositions. The reason for the difference is not clear, but the presence of hydrocarbon impurities in the titanium-tungsten target as a result of contamination during fabrication may result in a subsequent loss of film adhesion and the formation of the particles (11).

This particle problem would probably preclude the use of titanium-tungsten as a 'diffusion barrier' for gold/silicon due to the numerous defects and voids in the resultant films.

In an attempt to determine the concentrations of nitrogen, oxygen and carbon in the tungsten films and to establish a correlation between these impurity levels and the excellent barrier properties of the films, high-resolution Auger depth profile analyses were carried out. Figure 2 depicts the depth profile of DC magnetron sputtered tungsten in which the deposition was started in the stationary mode (no substrate rotation), and then continued with substrate rotation at 5 rpm. The change was made at about '28 minutes' on the time scale of the depth profile (after deposition of approximately half the tungsten film thickness).

From Figure 2 it will be seen that about 1.4 atomic per cent of nitrogen was present in the film deposited in the static mode and about 2.5 per cent in the film deposited with substrate rotation. The oxygen content of the film was essentially unchanged at about 8.5 atomic per cent throughout the thickness of the film (since the Auger data were taken at a relatively slow etch rate, it is likely that much of the oxygen signal was produced by oxidation of the film during Auger analysis due to the presence of trace amounts of oxygen even at low vacuum). The carbon concentration appeared to decrease slightly, from about 1.4 to about 1.3 atomic per cent with the transition from the stationary to the rotational mode of deposition. This decrease may not be significant since it is so small.

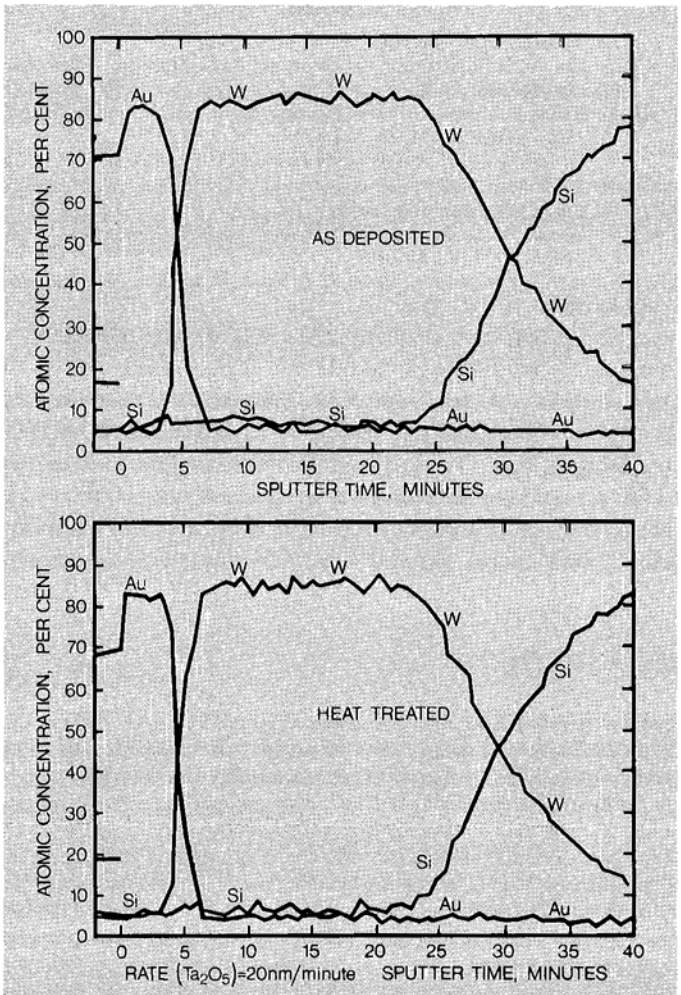

Fig. 1 Auger depth profiles of as-deposited (upper) and heat treated (lower) tungsten/gold films on silicon

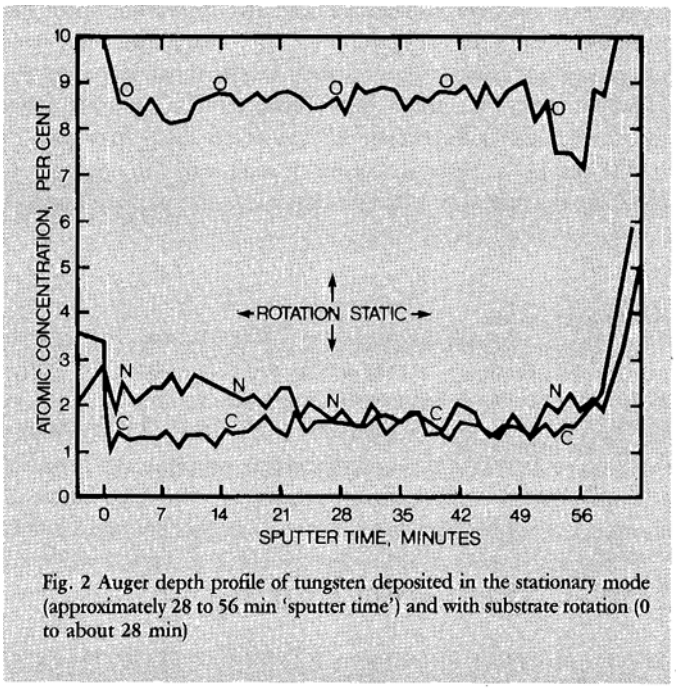

Fig. 2 Auger depth profile of tungsten deposited in the stationary mode (approximately 28 to 56 min 'sputter time') and with substrate rotation (0 to about 28 min)

Discussion and Summary

The above observations suggest that both DC magnetron sputtered titanium-tungsten and tungsten perform well as diffusion barriers between gold and silicon. However, when numerous depositions are carried out in series, a problem arises with the titanium-tungsten because of the deposition of some material in particulate form. This phenomenon was not observed with pure tungsten after a comparable number of depositions.

The cause of this difference in behaviour is not clear, but it is possible that intrinsic film stress levels give rise to loss of adhesion in the case of titanium-tungsten films. The typically high levels of hydrocarbon contaminants in the titanium-tungsten target (due to the method used in its fabrication), or 'gettering' of trace gaseous impurities from the vacuum ambient may produce greater stresses in the resultant films. The presence of hydrocarbon contaminants may also result in loss of film adhesion, and cause particulate 'fallout' from the shields and uniformity shapers used in the deposition systems. This phenomenon probably precludes the use of DC magnetron titanium-tungsten in deposition systems which have target-over-substrate configurations. The defects in these films, caused by the particles, render them unsuitable for applications requiring highly reliable thin films in interconnection or contact metallizations, such as in pacemaker diodes or integrated circuits used in aerospace applications.

The gold/tungsten system, on the other hand, does not appear to suffer from this disadvantage. Since DC magnetron sputtered tungsten has lower resistivity than, and can be etched in the same solutions (Freon-14 or hydrogen peroxide) as, titanium-tungsten, it appears to be a reasonable alternative to this material. However, more studies will be needed to confirm this suggestion.

Also unexplained is the reason for the apparent improvement in barrier properties of DC magnetron sputtered tungsten over RF diode sputtered titanium-tungsten. Auger analysis observations indicate a significantly higher level of nitrogen contamination throughout the DC magnetron deposited tungsten film than that reported (7) for the latter type of metallization.

A further query relates to whether or not this nitrogen level is sufficient to fill grain boundary voids. The answer to this is probably in the affirmative (1, 7). The data presented in Figure 2 suggest that the conditions of deposition, and specifically, whether it is conducted in stationary or rotational mode, may also play a role in impurity incorporation into the resultant films. The rotational mode yielded films with the greater nitrogen contamination.

There is thus some evidence that the incorporation of impurities during the deposition of DC magnetron sputtered tungsten films may account for their excellent barrier properties. However, the fact that these films tend to possess fewer microstructural defects than RF sputtered films may also be significant (12). More definitive studies will be necessary to elucidate the operative mechanism relevant to this phenomenon.

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Low-Carat Gold Plating

FUNDAMENTAL PROBLEMS EXPERIENCED WITH GOLD-SILVER SOLUTIONS

When the price of gold made its relatively sudden rise from US$350 to over $800 in late 1979/early 1980, manufacturers involved in decorative gold plating made considerable efforts to find ways of reducing the amount of gold which they required. These efforts included attempts to reduce the amounts of gold electrodeposited onto base metal articles such as chains, rings, bracelets and pendants in the production of costume jewellery. Savings were sought in two major directions: (a) by reducing the gold thickness to a minimum consistent with the performance requirements of the products, and (b) by reducing the caratage of part of the gold deposit through alloy plating.

The problems which were then encountered are well illustrated in a paper read to the 1981 International Precious Metals Institute 5th Annual Conference by F. R. Mazzotta of Avon Products, Inc., Mansfield, MA.. Avon Products investigated the feasibility not only of reducing gold thickness, but also of changing in part from 22-23 carat to 12-14 carat gold by co-deposition of silver with gold. Some of the difficulties experienced in plating gold-silver alloys were similar to those reported by others in this connection and with the electrodeposition of alloys generally. The particular merit of Mazzotta's contribution, however, is the frankness with which these problems are described. It serves, in fact, as a sober reminder that alloy plating on a mass-production scale is still a very difficult operation requiring considerable technological back-up and resources.

Mazzotta's results on the effect of gold deposit thickness on porosity, and thus susceptibility to base metal corrosion, agree well with those of D. G. Foulke (*Prod. Finish.*, 1967, **20**, (12), 38-44) and A. A. Khan (*Plating*, 1969, **56**, (12), 1374-1380). Thus, under production conditions using a normally prepared substrate surface and DC plating, a gold deposit thickness of 0.87 to 1.25 μm (35 to 50 microinches) represents a threshold, below which an unacceptable level of porosity and substrate corrosion will normally occur.

A 12-14 carat binary gold-silver plating system was chosen partly because of its ready availability from suppliers, and partly because it seemed simple in operation in comparison with an alternative ternary system. It was also known that it had been used commercially in the eyeglass frame and watch case industries (often regarded as more technologically based than the costume jewellery industry).

Brass samples were rack-plated to a nominal specification of 0.87 μm of 12-14 carat gold-silver alloy with a final deposit of 0.37 μm of 22-23 carat gold. Testing revealed the following fundamental problem areas:

(1) The two-layer gold deposit did not behave in the same manner as the 22-23 carat gold coating in all corrosion tests. The former showed a more orange colour after accelerated corrosion testing in aqueous media
(2) When rack plating from the gold-silver solution, not only did sample position influence deposit thickness through variations in current density, but also caratage which was found to vary between 8 and 14 (35 to 58 weight per cent gold)
(3) If the gold content in the gold-silver underlayer dropped to below 50 per cent (12 carat) the corrosion and tarnish resistances of the finished products were adversely affected
(4) Apart from its dependence on current density the caratage of the gold-silver underlayer was markedly affected by changes in solution temperature, gold and silver concentrations, and by bath agitation (this latter effect is particularly marked in a heavily-worked bath). These observations closely mirror those made by R. E. Harr and A. G. Cafferty (*Proc. Am. Electroplat. Soc.*, 1956, **43**, 67-69 and *Met. Finish.*, 1958, **56**, 55-57) in early experiments on a similar bath
(5) Beta backscatter techniques were found unsuitable for consistent monitoring of deposit thicknesses, because of the variations in caratage. Microcoulometric analysis showed promise in this regard, but equipment availability, test duration and the need for skilled interpretation of data mitigated against its use.

It appears, therefore, that serious and fundamental problems must be overcome before satisfactory production results can be expected from this system. C.L.